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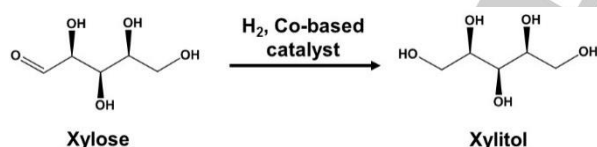
Selective hydrogenation of xylose to xylitol over Co/SiO₂ catalysts

Maïté Audemar,^[a] Ifrim Andreea Raluca,^[a] Tang Junhui,^[a] Adrian Ungureanu,^[b] François Jérôme,^[a] Sébastien Royer,^{[c]*} and Karine de Oliveira Vigier*^[a]

Dedication ((optional))

Abstract: Xylose can be selectively converted to xylitol in water, with an optimized yield of 98%, in the presence of a simple silica supported metallic cobalt - Co/SiO₂ - catalyst. This catalyst displays initial outstanding catalytic properties in proper solvent, the best one being pure water. Recyclability studies show a moderate deactivation of the catalyst, while selectivity to xylitol remains almost unchanged after 4 cycles, confirming the promising character of this catalyst formulation for the xylitol production process.

Xylose is a product issued from the hydrolysis of beechwood hemicelluloses. Different routes exist for the valorisation of xylose, amongst the selective hydrogenation to xylitol (scheme 1). Xylitol is an extensively used molecule in food, cosmetics, and pharmaceutical industry^[1-4]. Xylitol has then been identified as one of the top-twelve value added chemicals that can be obtained from biomass^[5]. As an example, xylitol is a valuable water soluble sweetener due to its atypical properties amongst, compared to sucrose, a higher sweetness strength and a lower energy capacity. Today, xylitol is widely incorporated in daily consumed products (chewing gums, chocolates, toothpastes, etc.)^[6]. With an estimated market of 340 M\$, xylitol is becoming the most popular “natural” sweeteners^[7]. Industrial production of xylitol by selective catalytic hydrogenation appears as an economically viable approach.



Scheme 1. Hydrogenation of xylose to xylitol.

Xylitol can be produced by catalytic hydrogenation in the presence of RANEY® nickel. Reaction is performed in liquid phase, under high hydrogen pressure and temperature in batch-

type reactors^[8]. Selectivity above 90%, at high conversion degree can be obtained at 80-130°C under 40-70 bar of H₂ (5 wt.% catalyst of the xylose mass present at 40-60 wt.% in water) in the presence of RANEY® nickel. Despite the high selectivity and activity reached using this catalyst, with economic advantages related to the use of noble metal free catalysts for the reaction, the intrinsic properties of the nickel, amongst toxicity and limited stability,^[8-9] makes the research of efficient catalyst substitutes. Indeed, the use of xylitol for food applications imply the absence of any trace of nickel in final product, nickel being recognized as a carcinogen compound. Most of recent studies were devoted to the study of supported noble metals, such as Ru, Rh and Pd, in monometallic or bimetallic catalytic systems, with the possible adding of dopants as Sn^[8-15] Ru appeared as the most efficient. Hernandez-Mejia *et al.*^[16] reported that xylose can be selectively converted to xylitol in the presence of rutile phase TiO₂ supported Ru (1 wt.%), despite the low surface area displayed by the rutile support. Authors then reported xylose yields higher than 90%, for a reaction performed in water at <140°C under 20 bar of H₂ and at a catalyst to xylose ratio (wt./wt.) of 1. Compared with rutile, better dispersion of Ru over anatase does not allowed to reach comparable activity, and conversion was not selective to xylitol. As recently reviewed by Delgado Arcano *et al.*, nickel and ruthenium catalysts then remains the most widely studied phases for the xylose to xylitol reaction, while titania is an adapted support^[15] Replacement of noble metal in catalytic formulation is however preferable due to limited resources, fluctuating costs, and consumption by high technology markets. Alternative catalysts, based on earth abundant transition metals such as cobalt, and in a lower extent copper, displaying lower toxicity than nickel are presenting satisfying activity and stability in water under neutral to basic conditions for some hydrogenation reactions^[17]. Then, for some hydrogenation of biomass derived molecules, cobalt formulations are considered as a viable formulations for hydrogenation reactions. Metallic cobalt indeed present interesting activity for the C=O bonds, as already observed for the selective conversion of cinnamaldehyde to cinnamyl alcohol,^[18-20] furfural to furfuryl alcohol,^[17,21] HMF hydroconversion,^[17,22] *etc.*

With this study, we demonstrated that, using a non noble metal catalyst based on cobalt supported on a commercially Aerosil® 380 silica, high yield to xylitol are obtained when reaction conditions are optimized, with a catalyst that can be reused at least three time before notable deactivation.

Silica supported cobalt oxide is prepared by Incipient Wetness Impregnation (IWI), starting from hydrated cobalt nitrate precursor, a classical and industrialized approach. Oxide precursor, Co₃O₄/SiO₂, is obtained by calcination of the solid at 500°C under air. Formation of Co₃O₄ phase is confirmed by XRD analysis (Figure 1(a)), with the presence of visible broad and poorly intense reflections corresponding to the awaited position (ICDD

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file n°42-1467). Considering the width of the reflections, awaited crystal domain size of the cobalt phase is relatively low (<10 nm). This results confirms that the impregnation used for the catalyst preparation is efficient to afford a high dispersion of the cobalt oxide phase.

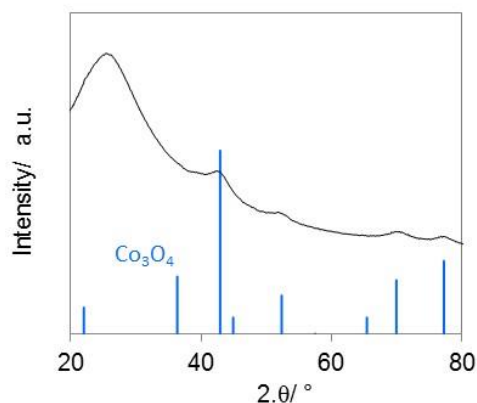


Figure 1. XRD analysis of Co/SiO₂ catalyst before and after reaction (vertical bars, reference ICDD 42-1467).

However, in view of the catalyst application, the catalyst is first reduced under H₂ flow at 500°C for 10h. Main characteristics of the reduced catalyst (Co/SiO₂) are presented in Table 1. Solid retains satisfying textural properties, mainly large surface area and large pore diameter, compatible for liquid phase catalytic reaction. In addition, the limited evolution of the textural properties indicate adequate stabilities of the support (Table 1).

Table 1. Main characteristic of the Co₂O₃/SiO₂ and reduced Co/SiO₂ materials.

	Co ₂ O ₃ /SiO ₂	Co/SiO ₂
XRD phase	Poorly crystallized Co ₃ O ₄	n.d. ^[a]
D _{part.} ^[b] nm	n. d. ^[a]	Aggregates 10 to >100 nm Crystals <20 nm
S _{BET} /c m ² g ⁻¹	185	169
V _p / cm ³ g ⁻¹	0.71	0.63
D _p / nm	15.0	14.7

[a] n.d.: not determined; [b] mean particle size obtained by TEM image observation; c, surface area (SBET), pore volume (V_p) and pore diameter (D_p) issued from N₂ physisorption at 77K.

Main Text Paragraphs----with Indentation.

Experimental Section

Experimental Details.

Acknowledgements ((optional))

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Keywords: keyword 1 • keyword 2 • keyword 3 • keyword 4 • keyword 5

- [1] ((Reference 1, Example for Journals:)) a) A. Author, B. Coauthor, *ChemSusChem* **2008**, *1*, 1-10; b) A. Author, B. Coauthor, *Angew. Chem.* **2006**, *118*, 1-5; *Angew. Chem. Int. Ed.* **2006**, *45*, 1-5.
- [2] ((Reference 2: Example for Books:)) J. W. Grate, G. C. Frye in *Sensors Update, Vol. 2* (Eds.: H. Baltes, W. Göpel, J. Hesse), Wiley-VCH, Weinheim, **1996**, pp. 10-20.
- [3] ...

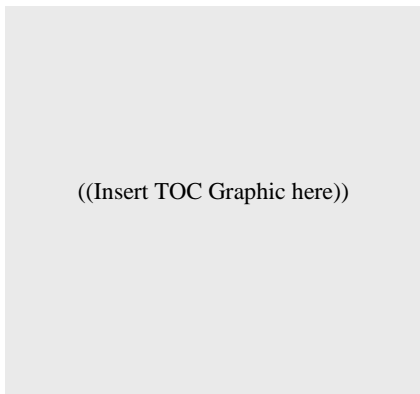
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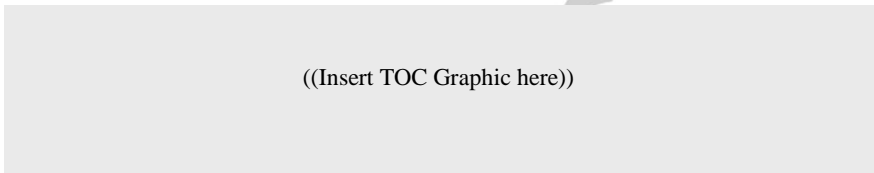
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